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Numerical study of metastability due to tunneling: The quantum string method

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Abstract

We generalize the string method, originally designed for the study of thermally activated rare events, to the calculation of quantum tunneling rates. This generalization is based on the formal analogy between quantum mechanics and statistical mechanics in the path-integral formalism. The quantum string method first locates the minimal action path (MAP), which is a smooth curve connecting two minima of the imaginary-time action in the space of imaginary-time trajectories. From the MAP, the saddle point of the action (called "the bounce") associated with the exponential factor for barrier tunneling probability is obtained and the pre-exponential factor (the ratio of determinants) for the tunneling rate evaluated using stochastic simulation. The quantum string method is implemented to calculate the bounce and rate of tunneling for the Mueller potential in two dimensions. The quantum problem is much more difficult than the thermally activated barrier crossing problem for the same potential. The model calculations show the string method to be an efficient numerical tool for the study of barrier tunneling in higher dimension, from the determination of the saddle point to the computation of the pre-exponential factor.

Keywords: String method; Barrier tunneling; Rate of decay; Quantum metastability

1. Introduction

One of the most important problems in statistical physics involves the rate of decay of a system [1] rendered unstable by thermally activated barrier crossing [2–4] and/or quantum barrier tunneling [5–7], and functional integrals represent a fundamental tool for studying these transition processes. However, numerical evaluation of the functional integrals has always been a challenge. Various numerical methods have been developed for finding pathways of thermally activated transitions or saddle points on potential energy landscapes [8–14]. Recently, the string method has been proposed for the numerical study of thermally activated rare events

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[15–19]. This method first locates the most probable transition pathway for a transition, which is the minimal energy path (MEP) connecting the initial and final (metastable) states in the configuration space. The transition rates can then be computed by numerically evaluating the fluctuations around the MEP. The string method bears some similarities with the nudged elastic band (NEB) method [12], which is also an efficient method for finding the MEP. In the NEB method, a chain of states is constructed between the initial and final states, and a spring interaction between adjacent states is added to ensure continuity of the path in mimicking an elastic band. In a force field comprising the normal component of the potential force and the tangential component of the spring force, the elastic band moves towards the MEP. Compared to the NEB method, the string method [15] uses an intrinsic description for the string, which is a continuous curve in the configuration space, discretized into a number of points moving according to the potential force. A reparametrization step is applied at every time step to ensure the continuity and the proper parametrization of the string, and the stationary curve approached by the evolving string gives the MEP.

The purpose of this paper is to generalize the string method to the study of quantum metastability caused by barrier tunneling. The theory for the rate of decay through barrier tunneling has been formulated using the imaginary-time functional integral techniques [5]. Essentially, the saddle point of the Euclidean action (called "the bounce" [5]) is first located in the space of imaginary-time trajectories (Feynman paths), and the rate of decay is then obtained by evaluating the relevant fluctuations around the saddle point. Technically, it is not a trivial task to locate the saddle point of the Euclidean action which is defined as a functional of the imaginary-time trajectories. In fact, only for a particle in one dimension can the saddle point be obtained in analytical form. Any generalization to particles in higher dimensions [20] or quantum fields [5] requires nontrivial analytical and/or numerical efforts.

To calculate the rate of a chemical reaction at low temperature, a quantum-mechanical transition state theory (TST) has been formulated [21,22], and a computational method called the centroid method [23,24] has been developed based on imaginary-time function integral. This method was tested and found to work well for transitions involving symmetric or weakly asymmetric potential barrier [23,24]. The centroid approximation, however, does not work well for potential of large asymmetry at low temperature [25]. A generalized quantum TST based on imaginary-time functional integral has been presented [25,26], where the saddle point of the Euclidean action, i.e., the bounce defined in Ref. [5], is identified with the transition state. To derive the transition rate in quantum TST, the functional integrals are usually evaluated within the harmonic (semiclassical) approximation where a normal mode expansion around the saddle point and the reactant minimum is used, and the corresponding rate theory has been formulated for zero temperature [5] and finite temperature [7].

Mathematically, the bounce is to be located at the maximum of the action along the minimal action path (MAP) [26], a curve defined in the space of imaginary-time trajectories, similar to the MEP in the configuration space. In Ref. [26], the NEB was employed to numerically find the MAP and the bounce. In this paper we will show that the string method can be used not only to efficiently locate the bounce for the exponential factor associated with the barrier tunneling probability, but also to evaluate the pre-exponential factor (the ratio of determinants) for the absolute value of the tunneling rate (within the semiclassical approximation). Our calculations are limited to the zero-temperature rate of barrier tunneling. The MAP is found numerically in the same way as the MEP, and the ratio of determinants is evaluated using stochastic simulation. Our numerical results show that the pre-exponential factor can contribute orders of magnitude to the absolute value of the rate, and hence cannot be ignored.

We want to point out that, while our approach may be regarded as a formal application of the string method, the barrier tunneling in multiple dimensions represents a problem that is much more difficult than the thermally activated barrier crossing in the same space. First of all, the space of imaginary-time trajectories is of infinite dimensions. Consequently, the landscape of the Euclidean action in that space is much more complicated than the potential energy landscape in the configuration space. For the Mueller potential [27,28] studied here, the potential itself is defined in the two-dimensional $\vec{q}$ space while the action is defined in the $\vec{q}(\tau)$ space of infinite dimensions (with τ denoting the imaginary time). As a consequence, the path traced out by the bounce, which corresponds to the saddle point of the action in the $\vec{q}(\tau)$ space, is very different from the MEP, which comprises the saddle point of the Mueller potential in the $\vec{q}$ space (see Section 4). In Ref. [20], the path traced out by the bounce is called the most probable escape path (MPEP). For the potential with certain

symmetry (equal-mass case), the MPEP should be straight and pass through the saddle point of the potential. However, when the symmetry is lost (unequal-mass case), the MPEP is curved and allocating it becomes nontrivial (a perturbation scheme was devised to obtain the MPEP) [20]. In Section 4 a fully numerical approach is presented for locating the curved MPEP associated with the Mueller potential. There is also a theoretical issue associated with the bounce in multiple dimensions. That the bounce is indeed a saddle point (i.e., the Hessian has one and only one negative eigenvalue) can be generally proved for tunneling in one dimension, but not for that in multiple dimensions [5]. Note that the formula for tunneling rate is based on the existence of one negative eigenvalue. Therefore, to justify the applicability of the rate formula, a numerical verification of the bounce as a saddle point is desired and the string method is shown to be capable of this. Finally, to obtain the absolute value of the rate, the pre-exponential factor, expressed as the ratio of Hessian determinants, has to be numerically computed. Due to the complicated landscape of the Euclidean action in the space of imaginary-time trajectories, the determinant ratio may turn out to be different from 1 by orders of magnitude, and hence have a nonnegligible contribution to the absolute value of the rate. For the Mueller potential here, the pre-exponential factor is found to be $\sim 10^6$. To the best of our knowledge, pre-exponential factor of such a magnitude has not been reported for thermally activated barrier crossing.

The paper is organized as follows. In Section 2 we first outline the string method for the numerical evaluation of thermal activation rate. We then show how this numerical method can be generalized to the evaluation of quantum tunneling rate. We emphasize that this generalization does not involve the physical crossover from thermal activation to quantum tunneling; it is entirely based on the formal similarity between the mathematical expressions for the two physically distinct rates. In Section 3 we review the bounce in one dimension, showing how extreme simplicity is rendered by the lowest space dimension. We then treat the quadratic-plus-cubic potential [29,30] to demonstrate the numerical precision of our scheme. In Section 4 we consider the nontrivial case of a particle in two dimensions, where the path traced out by the bounce displays an interesting correlation with the potential landscape. This correlation is expected to hold for higher dimensionality as well. We locate the bounce for the Mueller potential [27], which is a nontrivial test problem for transition path algorithms [28], and evaluate the corresponding tunneling rate. In Section 5 we conclude the paper with a few remarks.

2. Quantum string method

2.1. String method for thermally activated rare events

The string method was originally presented for the numerical study of thermal activation of metastable states [15]. Consider a system governed by the energy potential $V(\mathbf{q})$ in the overdamped regime, where $\mathbf{q}$ denotes the generalized coordinates $\{q_i\}$. The minima of $V(\mathbf{q})$ in the configuration space correspond to the metastable and stable states of the system. Given $\mathbf{q}_A$ and $\mathbf{q}_C$ as the two minima of V, the most probable fluctuation which can carry the system from $\mathbf{q}_A$ to $\mathbf{q}_C$ (or $\mathbf{q}_C$ to $\mathbf{q}_A$) corresponds to the lowest intervening saddle point $\mathbf{q}_B$ between these two minima, with the transition rate given by Refs. [2–4]

$$\Gamma_T(A \to C) = \frac{|\lambda_B|}{2\pi\eta}\left[\frac{|\det H(\mathbf{q}_B)|}{\det H(\mathbf{q}_A)}\right]^{-1/2} \exp\left\{\frac{\Delta V}{k_B T}\right\}, \tag{1}$$

where η is the frictional coefficient, $H(\mathbf{q})$ denotes the Hessian of $V(\mathbf{q})$, λ_B is the negative eigenvalue of $H(\mathbf{q}_B)$, and $\Delta V = V(\mathbf{q}_B) - V(\mathbf{q}_A)$ is the energy barrier. For the numerical evaluation of Γ_T, the MEP is defined as a smooth curve $\mathbf{q}^\star(s)$ in the configuration space. It connects $\mathbf{q}_A$ and $\mathbf{q}_C$, and satisfies

$$(\nabla V)^\perp(\mathbf{q}^\star) = 0, \tag{2}$$

where $(\nabla V)^\perp$ is the component of ∇V normal to the curve $\mathbf{q}^\star(s)$. Physically, the MEP is the most probable pathway for thermally activated transitions between $\mathbf{q}_A$ and $\mathbf{q}_C$; it goes through the saddle point between the two minima and follows the deterministic dynamics from the saddle point to either minimum. To numerically locate the MEP in the $\mathbf{q}$ space, a string $\mathbf{q}(s)$ (a smooth curve parametrized by the arc length s) is constructed with the only constraint that its two end points lie in the basins of attraction of $\mathbf{q}_A$ and $\mathbf{q}_C$ respectively.

The string is then evolved according to

$$\mathbf{q}_t = -\nabla V(\mathbf{q}) + \lambda\hat{\boldsymbol{\tau}}, \tag{3}$$

where λ is a Lagrange multiplier to enforce the parametrization of the string, and $\hat{\boldsymbol{\tau}}$ is the unit vector tangent to the string $\mathbf{q}(s)$ [17]. In practice, the string is discretized into a number of points $\{\mathbf{q}_i,\ i = 1, 2, \ldots, M\}$, and the above equation is solved by a time-splitting scheme. At each time step, every point is evolved according to the potential force $-\nabla V(\mathbf{q})$ by forward Euler or higher order Runge–kutta method. A reparametrization step is then applied to enforce the desired parametrization of the string, e.g., equal arc length. This is done by interpolation using cubic splines. The stationary solution of Eq. (3) satisfies Eq. (2) which defines the MEP. The saddle point corresponds to the maximum of the potential energy along the MEP. The negative eigenvalue λ_B and the corresponding eigenvector can be directly obtained from the MEP, and the ratio of the determinants in Eq. (1) can be numerically computed using a stochastic method [17].

The above scheme for the calculation of thermal activation rates has many applications, e.g., the condensation of a supersaturated vapor, the realignment of a magnetic domain [15,16], and the decay of persistent current in one-dimensional superconductor [31,32,19]. All of these transition processes occur when the system undergoes a fluctuation that is large enough to initiate the transition. Physically, the thermal activation rate Γ_T becomes practically unmeasurable as the temperature is sufficiently low ($k_B T \ll \Delta V$). However, even though thermodynamic fluctuations are suppressed at low temperature, a system can still be rendered unstable by quantum barrier tunneling [5]. The simplest example is a particle that escapes a potential well: it penetrates a potential barrier and emerges at the escape point with zero kinetic energy, after which it propagates classically.

2.2. Rate of barrier tunneling

The theory for the rate of barrier tunneling has been formulated and generalized using the imaginary-time functional integral techniques [5–7,21]. Here we show that the string method can be generalized to be an efficient numerical tool (the quantum string method) for the calculation of tunneling rates. In order to make concrete the formulation of the approach, below we consider a quantum particle that escapes a potential well through barrier tunneling. This particle case can be extended to a quantum field, where the classical false vacuum is rendered unstable by barrier tunneling [5].

Consider a particle of mass m moving in a one-dimensional potential $U(q)$ with two minima q_0 and q_1, one of which, q_1, is the absolute minimum (see Fig. 1a). Assume $U(q_0) = 0$ and q_1 is to the right of q_0 ($q_1 > q_0$). The normalized harmonic-oscillator ground state $\psi_g(q)$, centered at q_0, is $\psi_g(q) = (m\omega_0/\pi\hbar)^{1/4}$ $\exp[-m\omega_0(q - q_0)^2/2\hbar]$, where $\omega_0 = \sqrt{U''(q_0)/m}$ is the frequency locally defined at q_0. The ground-state energy is $\hbar\omega_0/2$. These familiar results can be derived from the imaginary-time propagator:

$$K(q_0, q_0; T) = \langle q_0|\mathrm{e}^{-\hat{H}T/\hbar}|q_0\rangle = \int [Dq(\tau)]\mathrm{e}^{-S/\hbar}, \tag{4}$$

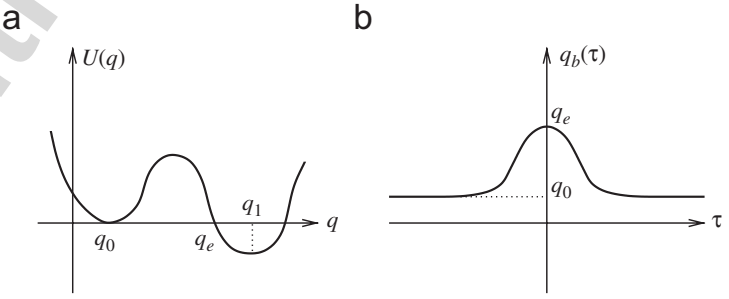

Fig. 1. (a) The potential in one dimension. The unstable ground state is centered at q_0. After penetrating the barrier, the particle emerges at the escape point q_e and propagates classically; (b) the bounce $q_b(\tau)$ for the imaginary-time classical equation of motion. In the inverted potential $-U(q)$, the particle begins at the top of the hill at q_0, turns around (i.e., bounces) at the classical turning point q_e, and returns to the top of the hill.

where T is the imaginary time duration, $\hat{H}$ is the Hamiltonian of the system,

$$S[q(\tau)] = \int_{-T/2}^{T/2} \mathrm{d}\tau \left\{ \frac{m}{2} \left(\frac{\mathrm{d}q}{\mathrm{d}\tau} \right)^2 + U[q(\tau)] \right\} \tag{5}$$

is the action, and $\int [Dq(\tau)]$ denotes the integration over functions $q(\tau)$ satisfying $q(-T/2) = q(T/2) = q_0$. Note that the imaginary-time (Euclidean) action $S[q(\tau)]$ can be obtained from the real-time (Minkowski) action

$$A[q(t)] = \int \mathrm{d}t \left\{ \frac{m}{2} \left[\frac{\mathrm{d}q(t)}{\mathrm{d}t} \right]^2 - U[q(t)] \right\}$$

through the formal substitution $t \to -\mathrm{i}\tau$ and $-\mathrm{i}A[q(t)] \to S[q(\tau)]$. Thus the equation of motion in imaginary time would involve an inverted potential, i.e., $U(q) \to -U(q)$. An expression for $K(q_0, q_0; T)$ in the limit of $T \to \infty$ (at zero-temperature) gives both the energy and the wavefunction of the lowest-lying energy eigenstate. In the semiclassical (small $\hbar$) limit, the functional integral for $K(q_0, q_0; T)$ is dominated by the stationary points of the action S, denoted by $\bar{q}(\tau)$, that satisfy the imaginary-time equation of motion

$$\left[\frac{\delta S}{\delta q} \right]_{\bar{q}} = -m \frac{\mathrm{d}^2 \bar{q}}{\mathrm{d}\tau^2} + U'(\bar{q}) = 0$$

with the boundary condition $\bar{q}(-T/2) = \bar{q}(T/2) = q_0$. There are two solutions: one is $\bar{q}(\tau) = q_0$, at which the Hessian of S, $-m\partial_\tau^2 + U''(q_0)$, has positive eigenvalues only, and the other is the so-called bounce $q_b(\tau)$, at which the Hessian of S, $-m\partial_\tau^2 + U''[q_b(\tau)]$, has a zero eigenvalue plus a negative eigenvalue. The zero eigenvalue comes from the time-translation symmetry and the negative eigenvalue makes $q_b(\tau)$ a saddle point of $S[q(\tau)]$. By following the bounce $q_b(\tau)$ in time, the quantum particle would initially stay at q_0 for a long time, on the order of T, then make a brief excursion to the escape point q_e (separated from q_0 by a potential barrier, with $U(q_e) = U(q_0)$) in a time of order $1/\omega_0$, and finally return to q_0 and remain there for another duration of order T (see Fig. 1b). This process is called a "bounce". Here q_e is the escape point at which the quantum tunneling particle leaves the barrier. Physically $q_b(\tau)$ characterizes a fluctuation large enough to accomplish the barrier penetration. (For more details, see Section 3.) Using the two stationary points of S in the semiclassical approximation with a proper analytic continuation [5], the propagator in Eq. (4) is obtained as

$$|\psi_g(q_0)|^2 \mathrm{e}^{-E_g T/\hbar} = (m\omega_0/\pi\hbar)^{1/2} \mathrm{e}^{-\omega_0 T/2} \mathrm{e}^{-\mathrm{i}\mathrm{Im}E_g T/\hbar} \tag{6}$$

which gives $|\psi_g(q_0)|^2 = (m\omega_0/\pi\hbar)^{1/2}$, the ground-state energy $\hbar\omega_0/2$, and an imaginary part of the energy $\mathrm{Im}\, E_g$. Physically, $\mathrm{Im}\, E_g$ (<0) is responsible for the decay of the metastable "ground state" centered at q_0, with the decay rate $\Gamma_Q = -2\mathrm{Im}\, E_g/\hbar$:

$$\Gamma_Q = \omega_0 \sqrt{\frac{S_b}{2\pi\hbar}} \left[\frac{U''(q_0)|\det' H[q_b(\tau)]|}{\det H(q_0)} \right]^{-1/2} \mathrm{e}^{-S_b/\hbar}, \tag{7}$$

where H denotes the Hessian of S: $H[q(\tau)] = -m\partial_\tau^2 + U''[q(\tau)]$, $S_b \equiv S[q_b(\tau)]$ is the action associated with the bounce $q_b(\tau)$, and $\det'$ indicates that the zero eigenvalue is to be omitted in computing the determinant.

2.3. Numerical implementation of quantum string method

Here we generalize the string method to the numerical evaluation of quantum tunneling rate. It is worth emphasizing that this generalization does not involve the physical crossover from thermal activation to quantum tunneling, which has been of considerable interest for decades; it is entirely based on the formal similarity between the mathematical expressions for the two physically distinct rates: the thermal rate Γ_T in Eq. (1) and the quantum rate Γ_Q in Eq. (7) [33]. To display such formal similarity, we write the action $S[q(\tau)]$ in Eq. (5) as $S(\mathbf{q})$, where the vector $\mathbf{q}$ represents the coordinates in the $q(\tau)$-function space ($\mathbf{q}$ space). (Computationally, there are always a large but finite number of these coordinates.) As the quantum physics is governed by the action, the MAP is defined as a smooth curve $\mathbf{q}^\star(s)$ in the $\mathbf{q}$ space [26]. Being a formal

generalization of the MEP, the MAP connects the two minima of S, $\mathbf{q}_0$ and $\mathbf{q}_1$, with intrinsic parametrization such as arc length s, satisfying

$$(\nabla S)^{\perp}(\mathbf{q}^{\star}) = 0, \tag{8}$$

where $(\nabla S)^{\perp}$ is the component of ∇S normal to the curve $\mathbf{q}^{\star}(s)$. Here, $\mathbf{q}_0$ and $\mathbf{q}_1$ correspond to $\bar{q}(\tau) = q_0$ and $\bar{q}(\tau) = q_1$, respectively. (A slightly different choice for $\mathbf{q}_1$ is also possible, corresponding to a $\bar{q}(\tau)$ profile with $\bar{q}(\tau) = q_1$ in most of the τ-interval $[-T/2, T/2]$ and $\bar{q}(-T/2) = \bar{q}(T/2) = q_0$.) The saddle point of S is obtained as the point $\mathbf{q}_b$ which has the maximum value of S along the MAP. This corresponds to the bounce $q_b(\tau)$. To numerically locate the MAP in the $\mathbf{q}$ space, a string $\mathbf{q}(s, t)$ connecting $\mathbf{q}_0$ and $\mathbf{q}_1$ is evolved according to Eq. (3) with V replaced by S. The stationary solution is the MAP defined by Eq. (8).

The ratio of determinants in Eq. (7) can be numerically obtained as follows:

(1) From the MAP $\mathbf{q}^{\star}(s)$ parametrized by the arc length s, the eigenvector $\mathbf{u}_b^{(1)}$ corresponding to the negative eigenvalue $\lambda_b^{(1)}$ of the Hessian $H(\mathbf{q}_b)$ can be obtained by evaluating $\mathrm{d}\mathbf{q}^{\star}(s)/\mathrm{d}s$ at the saddle point $\mathbf{q}_b$, followed by a normalization. $\lambda_b^{(1)}$ is then computed from $\lambda_b^{(1)} = [\mathbf{u}_b^{(1)}]^{\mathrm{T}} H(\mathbf{q}_b)\mathbf{u}_b^{(1)}$.
(2) The eigenvector $\mathbf{u}_b^{(2)}$ corresponding to the zero eigenvalue $\lambda_b^{(2)}$ of the Hessian $H(\mathbf{q}_b)$ can be obtained by evaluating $\partial_{\tau} q_b(\tau)$ from $\mathbf{q}_b$, followed by a normalization.
(3) The Hessian $H(\mathbf{q}_b)$ is modified to give a positive definite matrix $\tilde{H}(\mathbf{q}_b)$:

$$\tilde{H}(\mathbf{q}_b) = H(\mathbf{q}_b) + 2|\lambda_b^{(1)}|[\mathbf{u}_b^{(1)}][\mathbf{u}_b^{(1)}]^{\mathrm{T}} + [\mathbf{u}_b^{(2)}][\mathbf{u}_b^{(2)}]^{\mathrm{T}}, \tag{9}$$

whose determinant $\det \tilde{H}(\mathbf{q}_b)$ equals $|\det' H(\mathbf{q}_b)|$.
(4) In order to compute the ratio of determinants $\det \tilde{H}(\mathbf{q}_b)/\det H(\mathbf{q}_0)$, a harmonic potential parametrized by α $(0 \leqslant \alpha \leqslant 1)$ is constructed as

$$U^{\alpha}(\mathbf{q}) = \tfrac{1}{2}\mathbf{q}^{\mathrm{T}}[(1-\alpha)\tilde{H}(\mathbf{q}_b) + \alpha H(\mathbf{q}_0)]\mathbf{q} \tag{10}$$

in the N-dimensional $\mathbf{q}$ space. It can be shown [17] that

$$\frac{\det \tilde{H}(\mathbf{q}_b)}{\det H(\mathbf{q}_0)} = \exp\left[2\int_0^1 \mathrm{d}\alpha Q(\alpha)\right], \tag{11}$$

where $Q(\alpha)$ is the expectation value

$$Q(\alpha) = \frac{1}{Z(\alpha)}\int \mathrm{d}\mathbf{q}\left\{\frac{1}{2}\mathbf{q}^{\mathrm{T}}[\tilde{H}(\mathbf{q}_b) - H(\mathbf{q}_0)]\mathbf{q}\right\}\mathrm{e}^{-U^{\alpha}(\mathbf{q})} \tag{12}$$

in which $Z(\alpha)$ is the partition function

$$Z(\alpha) = \int \mathrm{d}\mathbf{q}\, \exp[-U^{\alpha}(\mathbf{q})]. \tag{13}$$

To evaluate the determinant ratio in Eq. (11), the canonical ensemble governed by the potential $U^{\alpha}(\mathbf{q})$ is generated by solving the stochastic equation

$$\dot{\mathbf{q}} = -\nabla U^{\alpha}(\mathbf{q}) + \boldsymbol{\zeta}, \tag{14}$$

where $\boldsymbol{\zeta}(t)$ is a white noise satisfying $\langle \zeta_i(t)\zeta_j(t')\rangle = 2\delta_{ij}\delta(t-t')$, and the expectation value $Q(\alpha)$ is then numerically measured according to Eq. (12) [17].

3. Tunneling in one dimension

For a particle in one dimension, the bounce $q_b(\tau)$ is a solution of the imaginary-time classical equation of motion

$$m\frac{\mathrm{d}^2 q}{\mathrm{d}\tau^2} = U'(q), \tag{15}$$

subject to the boundary condition $q(-T/2) = q(T/2) = q_0$ for $T \to \infty$. The qualitative behavior of $q_b(\tau)$ is suggested by the analogy with the equation of motion for a particle of mass m in the inverted potential $-U(q)$,

in which q_0 now corresponds to the top of the hill and q_e to the classical turning point. The particle would spend most of its time at q_0 (due to zero velocity), but, in the course of an arbitrarily long interval of time, it would make a brief excursion to the point q_e and then return to q_0 (see Fig. 1b).

The bounce $q_b(\tau)$ shown in Fig. 1b is centered at $\tau_c = 0$ along the τ axis. Because of the time-translation invariance of the action, the bounces are also given by $q_b(\tau - \tau_c)$, where τ_c is an arbitrary center of the bounce. This symmetry property leads to a zero eigenvalue for the Hessian of S at $q_b(\tau)$, $-m\partial_\tau^2 + U''[q_b(\tau)]$. The corresponding eigenfunction is given by

$$u_b^{(2)}(\tau) = \sqrt{\frac{m}{S_b}}\frac{\mathrm{d}q_b(\tau)}{\mathrm{d}\tau}, \tag{16}$$

where $\sqrt{m/S_b}$ is the normalization factor derived from the action of the bounce

$$S_b = \int_{-T/2}^{T/2} \mathrm{d}\tau \left\{ \frac{m}{2}\left[\frac{\mathrm{d}q_b(\tau)}{\mathrm{d}\tau}\right]^2 + U[q_b(\tau)] \right\} \tag{17}$$

and the constant of motion

$$\frac{m}{2}\left[\frac{\mathrm{d}q_b(\tau)}{\mathrm{d}\tau}\right]^2 - U[q_b(\tau)] = -U(q_0) = 0. \tag{18}$$

Note that $\mathrm{d}q_b/\mathrm{d}\tau$ vanishes at the center of the bounce where q reaches q_e. Therefore, $u_b^{(2)}(\tau)$ has a node and cannot be the eigenfunction with the lowest eigenvalue: there must be a nodeless eigenfunction, $u_b^{(1)}(\tau)$, with a negative eigenvalue. This implies that the bounce is not a minimum of the action but a saddle point. The negative eigenvalue requires a proper analytical continuation in evaluating the functional integral in (4). This leads to a complex value of the energy in Eq. (6).

Using the constant of motion, the bounce action can be reduced to the form

$$S_b = \int_{-T/2}^{T/2} \mathrm{d}\tau \left\{ m\left[\frac{\mathrm{d}q_b(\tau)}{\mathrm{d}\tau}\right]^2 \right\} = 2\int_{q_0}^{q_e} \mathrm{d}q\sqrt{2mU(q)}. \tag{19}$$

It is seen that $\mathrm{e}^{-S_b/2\hbar}$ is the familiar WKB exponential factor for the amplitude of tunneling wave. Accordingly, $\mathrm{e}^{-S_b/\hbar}$ is the exponential factor for the current density of the tunneling wave, which is directly related to the rate of decay as reflected in Eq. (7). We want to remark that for one-dimensional quantum mechanics, the tunneling rate (7) derived from functional integral agrees with that obtained by standard WKB method of wave mechanics [5].

In order to demonstrate the validity and precision of the quantum string method, numerical calculations have been carried out to reproduce the bounce action and determinant ratio for the quadratic-plus-cubic potential, an important model potential for the study of quantum metastability [29,30]. It has been shown that the centroid method does not work well for such a potential of large asymmetry at low temperature [25]. For simplicity, we work with the scaled action

$$S[q(\tau)] = \int \mathrm{d}\tau \left[\frac{1}{2}\left(\frac{\mathrm{d}q}{\mathrm{d}\tau}\right)^2 + \frac{1}{2}q^2(1-q)\right]. \tag{20}$$

The potential $q^2(1-q)/2$ in action (20) has $q_0 = 0$ as the metastable minimum and $q_e = 1$ as the escape point. For computational purpose, this potential is modified in the region of $q \gg q_e$ to generate another (lower) minimum at q_1 ($\gg q_e$). Numerically, the two potential minima q_0 and q_1 are used to fix the ends of the evolving string in the $q(\tau)$-function space. The stationary solution for the string evolution equation is the MAP, from which the saddle point of $S[q(\tau)]$, i.e., the bounce $q_b(\tau)$, can be obtained. Since the potential profile is untouched in the classically forbidden region ($q_0 \leqslant q \leqslant q_e$), the bounce so obtained is not affected by the potential modification far away. The bounce action $S_b \equiv S[q_b(\tau)]$ is obtained to be 0.5337, very close to the

exact result $\frac{8}{15}$. The determinant ratio

$$\frac{|\det' H[q_b(\tau)]|}{\det H(q_0)} = \frac{|\det'[-\partial^2/\partial\tau^2 + 1 - 3q_b(\tau)]|}{\det(-\partial^2/\partial\tau^2 + 1)} \tag{21}$$

is obtained to be 0.0142, close to the analytic result $\frac{1}{60}$ [29,30]. These results are obtained using $N = 200$ in discretizing $-T/2 \leqslant \tau \leqslant T/2$, $M = 200$ in discretizing the string, and the total imaginary time duration $T = 20$. Better agreement with the exact results can certainly be achieved by using longer imaginary time duration, vector space of higher dimensionality, finer resolution in discretizing the string, and more realizations in the stochastic simulation for measuring $Q(\alpha)$.

4. Tunneling in multiple dimensions

The bounce in one dimension is in fact extremely simple because the path is constrained by the lowest space dimension. Below we consider the barrier penetration in two dimensions, where the path traced out by the bounce displays an interesting correlation with the potential landscape. The potential we use is the Mueller potential [27] which is a nontrivial test problem for transition path algorithms [28]. The space coordinates are denoted by $\vec{q} \equiv (x, y)$. The explicit form for the potential $U(\vec{q})$ is given in Appendix A, and the dimensionless action is

$$S[\vec{q}(\tau)] = \int \mathrm{d}\tau \left[\frac{1}{2}\left(\frac{\mathrm{d}\vec{q}}{\mathrm{d}\tau}\right)^2 + U(\vec{q})\right]. \tag{22}$$

The bounce that we are going to locate controls the metastability of the quantum state centered at $\vec{q}_0$, a relative minimum of $U(\vec{q})$ (see Fig. 2). Unlike in one dimension, here $U(\vec{q}) = U(\vec{q}_0)$ determines a continuous level curve that encloses the absolute minimum $\vec{q}_1$. It is at this level curve that the escape point $\vec{q}_e$ is to be determined. Similar to the case in one dimension, the two minima $\vec{q}_0$ and $\vec{q}_1$ are used to fix the two ends of the evolving string in the $\vec{q}(\tau)$-function space. The stationary solution for the string evolution equation gives the MAP from which the saddle point of $S[\vec{q}(\tau)]$, i.e., the bounce $\vec{q}_b(\tau)$, is obtained. To verify that the bounce is entirely determined by the potential profile in the classically forbidden region, we have locally distorted the potential inside the region enclosed by the level curve of $U(\vec{q}) = U(\vec{q}_0)$, and calculated the MAP.

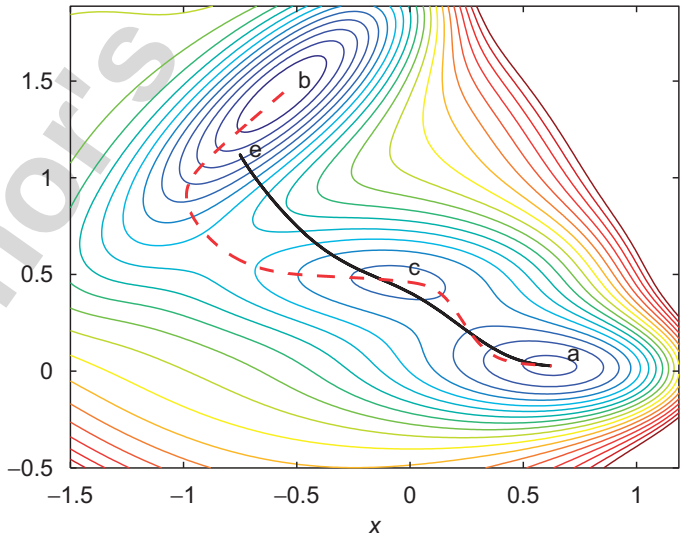

Fig. 2. The path traced out by the bounce $\vec{q}_b(\tau)$ for the Mueller potential (thick solid line). The bounce starts from the relative minimum $\vec{q}_0$ (point a), turns around at the escape point $\vec{q}_e$ (point e), and returns to $\vec{q}_0$ along the same path. The absolute minimum $\vec{q}_1$ (point b) is enclosed by the level curve of $U(\vec{q}) = U(\vec{q}_0)$, at which the escape point is located. The MEP is also plotted for comparison (thick dashed line). It goes from the relative minimum $\vec{q}_0$ to the absolute minimum $\vec{q}_1$, passing through another relative minimum $\vec{q}_2$ (point c) and two saddle points of $U(\vec{q})$.

The numerical results show the bounce remains unchanged. The action of the bounce,

$$S_b = \int \mathrm{d}\tau \left\{ \frac{1}{2} \left[\frac{\mathrm{d}\vec{q}_b(\tau)}{\mathrm{d}\tau} \right]^2 + U[\vec{q}_b(\tau)] - U(\vec{q}_0) \right\} \tag{23}$$

is found to be 29.54. Note that only the potential energy difference $U(\vec{q}_b) - U(\vec{q}_0)$ is counted in S_b.

In essence, to locate the bounce in the $\vec{q}(\tau)$-function space is to locate in the (x, y) space the path traced out by the bounce, because along this path the velocity $\mathrm{d}\vec{q}/\mathrm{d}\tau$ is already fixed by the constant of motion

$$\frac{1}{2} \left[\frac{\mathrm{d}\vec{q}_b(\tau)}{\mathrm{d}\tau} \right]^2 - U[\vec{q}_b(\tau)] = -U(\vec{q}_0) \tag{24}$$

associated with bounce. Physically, the path traced out by the bounce in the (x, y) space is the path along which the amplitude of the tunneling wave is least damped, so-called the most probable escape path in Ref. [20]. It corresponds to the minimum of the line-integral action

$$\int_{\vec{q}_0}^{\vec{\sigma}} \mathrm{d}l \sqrt{2[U(\vec{q}) - U(\vec{q}_0)]}, \tag{25}$$

where $\mathrm{d}l = \sqrt{\mathrm{d}\vec{q} \cdot \mathrm{d}\vec{q}}$, $\vec{\sigma}$ is some point at the level curve of $U(\vec{q}) = U(\vec{q}_0)$, and the integral is over some path connecting $\vec{q}_0$ and $\vec{\sigma}$. Here, the complexity due to the multiple space dimensions is obvious: the path traced out by the bounce is to be determined by the potential landscape while in one dimension the path is simply a line between the metastable minimum and the escape point.

According to the line integral (25), the path traced out by the bounce must display a compromise between the minimization of the arc length $\int \mathrm{d}l$ and that of the potential energy U. It is interesting to compare the bounce with the MEP for $U(\vec{q})$, the latter defined by $(\nabla_{\vec{q}} U)^{\perp}(\vec{q}^{\star}) = 0$ according to Eq. (2). As shown in Fig. 2, the MEP connects the relative minimum $\vec{q}_0$ to the absolute minimum $\vec{q}_1$, passing through another relative minimum (denoted by $\vec{q}_2$) and two saddle points of $U(\vec{q})$. In particular, between $\vec{q}_0$ and $\vec{q}_2$ the MEP is relatively straight and thus approximately minimizes $\int \mathrm{d}l$. Consequently, the path traced out by the bounce is close to this segment of the MEP. However, between $\vec{q}_2$ and $\vec{q}_1$ the MEP is strongly curved and lies far away from the path traced out by the bounce. In fact the relatively straight path traced out by the bounce indicates that the minimization of the arc length $\int \mathrm{d}l$ is dominant in this part. The above correlation between the bounce and the potential landscape is expected to hold for higher dimensionality as well.

To obtain the rate of decay associated with the bounce $\vec{q}_b(\tau)$, we need to evaluate the determinant ratio

$$\frac{|\det' H[\vec{q}_b(\tau)]|}{\det H(\vec{q}_0)} = \frac{|\det'\{-\partial^2/\partial\tau^2 + \nabla^2_{\vec{q}} U[\vec{q}_b(\tau)]\}|}{\det\{-\partial^2/\partial\tau^2 + \nabla^2_{\vec{q}} U(\vec{q}_0)\}} \tag{26}$$

following the procedure outlined in Section 2.3. Again the vector $\mathbf{q}$ is used to represent $\vec{q}(\tau)$, and the MAP is regarded as a smooth curve in the $\mathbf{q}$ space. The vector tangent to the MAP at the saddle point (the bounce, denoted by $\mathbf{q}_b$) gives the first eigenvector of $H(\mathbf{q}_b)$, $\mathbf{u}_b^{(1)}$, corresponding to the only negative eigenvalue $\lambda_b^{(1)}$. There is also the eigenvector $\mathbf{u}_b^{(2)}$ corresponding to the zero eigenvalue due to the time-translation invariance. Readily obtained from the MAP, these eigenvectors are used to modify the Hessian $H(\mathbf{q}_b)$ such that a positive definite matrix

$$\tilde{H}(\mathbf{q}_b) = H(\mathbf{q}_b) + 2|\lambda_b^{(1)}|[\mathbf{u}_b^{(1)}][\mathbf{u}_b^{(1)}]^{\mathrm{T}} + \lambda[\mathbf{u}_b^{(2)}][\mathbf{u}_b^{(2)}]^{\mathrm{T}} \tag{27}$$

is constructed. The calculation of the ratio of $\det \tilde{H}(\mathbf{q}_b)$ to $\det H(\mathbf{q}_0)$ follows the procedure outlined in Section 2.3. Finally the determinant ratio in Eq. (26) is obtained as

$$\frac{1}{\lambda} \frac{\det \tilde{H}(\mathbf{q}_b)}{\det H(\mathbf{q}_0)} = \frac{1}{\lambda} \exp\left[2 \int_0^1 \mathrm{d}\alpha Q(\alpha) \right] \tag{28}$$

with $\lambda^{-1} \det \tilde{H}(\mathbf{q}_b) = |\det' H(\mathbf{q}_b)| \equiv |\det' H[\vec{q}_b(\tau)]|$ and $\det H(\mathbf{q}_0) \equiv \det H(\vec{q}_0)$, and the numerical results for $Q(\alpha)$ are plotted in Fig. 3. Here different choices of λ are used. The derivatives and the Hessian of the Mueller potential are on the order of $O(100)$, so we have used $\lambda = 50$, 200, 400, and 800, respectively, in our

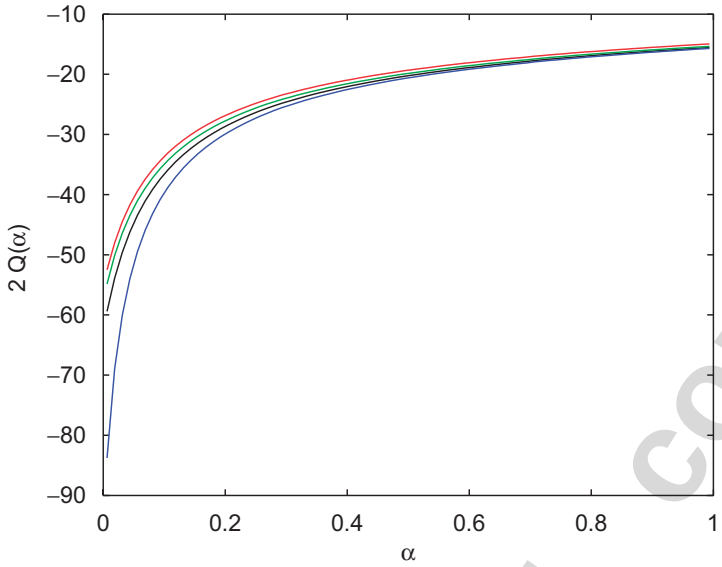

Fig. 3. Q in Eq. (28), plotted as a function of α. The derivatives and the Hessian of the Mueller potential are on the order of $O(100)$. So when the Hessian of the action at the bounce is modified according to Eq. (27), the values of 50, 200, 400, and 800 are used for λ. The different curves from bottom to top correspond to these different values of λ.

calculation. The different curves from bottom to top in Fig. 3 correspond to these values, and they agree very well: the logarithms of the ratio in Eq. (26) calculated from these curves are −29.04, −28.97, −28.95 and −28.95, respectively.

Based on the numerical results above, the (dimensionless) rate of decay associated with the bounce $\vec{q}_b$,

$$\Gamma_Q = \sqrt{\frac{S_b\hat{S}}{2\pi\hbar}}\left[\frac{|\det' H[\vec{q}_b(\tau)]|}{\det H(\vec{q}_0)}\right]^{-1/2} e^{-S_b\hat{S}/\hbar} \tag{29}$$

is given by

$$\sqrt{\frac{29.54}{2\pi}}\sqrt{\frac{\hat{S}}{\hbar}}[e^{-29.0}]^{-1/2}e^{-29.54\hat{S}/\hbar}, \tag{30}$$

where $\hat{S}$ is the unit in which the dimensionless actions S in Eq. (22) and S_b in Eq. (23) are defined. (While S is introduced for the convenience of calculations, the physically important dimensionless quantity is $S\hat{S}/\hbar$.) Our numerical results show that the pre-exponential factor can contribute orders of magnitude to the absolute value of the rate, and hence cannot be ignored.

5. Concluding remarks

It should be noted that the usual wave-mechanical WKB method becomes very difficult to implement in higher dimensional quantum particle problems [20], and it is precisely in such problems that the present approach can offer an efficient numerical tool in finding the path of least resistance to tunneling, and on that basis calculate the relevant tunneling rate.

It should also be noted that as a tool for the numerical evaluation of tunneling rate in the path-integral formalism, the quantum string method is directly generalizable to field theoretic problems, requiring only additional computational resources. The computational task for a quantum field in d-dimensional space is equivalent to that for a classical field in $(d+1)$-dimensional space [5]. Therefore, the quantum version of the string method can be numerically implemented as its original classical version for a higher dimensional system.

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Appendix A. The Mueller potential

The Mueller potential is of the form

$$U(\vec{q}) \equiv U(x,y) = \sum_{i=1}^{4} A_i e^{a_i(x-x_i)^2 + b_i(x-x_i)(y-y_i) + c_i(y-y_i)^2} \tag{A.1}$$

with the parameters

$$\begin{aligned}
&(A_1, A_2, A_3, A_4) = (-200, -100, -170, 15),\\
&(a_1, a_2, a_3, a_4) = (-1, -1, -6.5, 0.7),\\
&(b_1, b_2, b_3, b_4) = (0, 0, 11, 0.6),\\
&(c_1, c_2, c_3, c_4) = (-10, -10, -6.5, 0.7),\\
&(x_1, x_2, x_3, x_4) = (1, 0, -0.5, -1),\\
&(y_1, y_2, y_3, y_4) = (0, 0.5, 1.5, 1).
\end{aligned}$$

References

[1] P. Hänggi, P. Talkner, M. Borkovec, Rev. Mod. Phys. 62 (1990) 251.
[2] H.A. Kramers, Physica 7 (1940) 284.
[3] R. Landauer, J.A. Swanson, Phys. Rev. 121 (1961) 1668.
[4] J.S. Langer, Ann. Phys. (NY) 41 (1967) 108;
J.S. Langer, Phys. Rev. Lett. 21 (1968) 973.
[5] S. Coleman, Phys. Rev. D 15 (1977) 2929;
C.G. Callan Jr., S. Coleman, Phys. Rev. D 16 (1977) 1762.
[6] A.O. Caldeira, A.J. Leggett, Phys. Rev. Lett. 46 (1981) 211.
[7] I. Affleck, Phys. Rev. Lett. 46 (1981) 388.
[8] R. Elber, M. Karplus, Chem. Phys. Lett. 139 (1987) 375.
[9] R. Czerminski, R. Elber, Int. J. Quantum Chem. 24 (1990) 167.
[10] C. Choi, R. Elber, J. Chem. Phys. 94 (1991) 751.
[11] S. Fischer, M. Karplus, Chem. Phys. Lett. 194 (1992) 252.
[12] H. Jónsson, G. Mills, K.W. Jacpbsen, Nudged elastic band method for finding minimum energy paths of transitions, in: B.J. Berne, G. Ciccotti, D.F. Coker (Eds.), Classical and Quantum Dynamics in Condensed Phase Simulations, World Scientific, Singapore, 1998, p. 385.
[13] I.V. Ionova, E.A. Carter, J. Chem. Phys. 98 (1993) 6377.
[14] G. Henkelman, H. Jónsson, J. Chem. Phys. 111 (1999) 7010.
[15] W. E, W. Ren, E. Vanden-Eijnden, Phys. Rev. B 66 (2002) 052301.
[16] W. E, W. Ren, E. Vanden-Eijnden, J. Appl. Phys. 93 (2003) 2275.
[17] W. E, W. Ren, E. Vanden-Eijnden, Zero-temperature String Method for the Study of Rare Events, unpublished
[18] W. Ren, Comm. Math. Sci. 1 (2003) 377.
[19] T. Qian, W. Ren, P. Sheng, Phys. Rev. B 72 (2005) 014512.
[20] T. Banks, C.M. Bender, T.T. Wu, Phys. Rev. D 8 (1973) 3346;
T. Banks, C.M. Bender, Phys. Rev. D 8 (1973) 3366.
[21] W.H. Miller, J. Chem. Phys. 61 (1974) 1823.
[22] For a comprehensive review on TST, see D.G. Truhlar, B.C. Garrett, S.J. Klippenstein, J. Phys. Chem. 100 (1996) 12771.
[23] M.J. Gillan, J. Phys. C 20 (1987) 3621.
[24] G.A. Voth, D. Chandler, W.H. Miller, J. Chem. Phys. 91 (1989) 7749.
[25] D.E. Makarov, M. Topaler, Phys. Rev. E 52 (1995) 178.
[26] G. Mills, G.K. Schenter, D.E. Makarov, H. Jonsson, Chem. Phys. Lett. 278 (1997) 91.

[27] K. Mueller, Angew. Chem. 19 (1980) 1;
K. Mueller, L.D. Brown, Theoret. Chim. Acta 53 (1979) 78.
[28] See, for example, R. Olender, R. Elber, J. Chem. Phys. 105 (1996) 9299.
[29] A.O. Caldeira, A.J. Leggett, Ann. Phys. (N.Y.) 149 (1983) 374.
[30] M. Ueda, A.J. Leggett, Phys. Rev. Lett. 80 (1998) 1576.
[31] J.S. Langer, V. Ambegaokar, Phys. Rev. 164 (1967) 498.
[32] D.E. McCumber, B.I. Halperin, Phys. Rev. B 1 (1970) 1054.
[33] Physically, however, the MAP reduces to the MEP above the quantum-classical crossover temperature. But our calculations are for the zero-temperature MAP and rate only.